

REMARKS

Claims 1-20 are pending in this application. In view of the following remarks, reconsideration and allowance of claims 1-20 are respectfully requested.

Interview

The courtesies extended to Applicants' representative by Examiners Graham and Marcheschi at the interview held February 3, 2011, are appreciated. The reasons presented at the interview as warranting favorable action are incorporated into the remarks below, which constitute Applicants' record of the interview.

35 U.S.C. §103(a) Rejections

The following claims were rejected under 35 U.S.C. §103(a) as allegedly being obvious: (1) claims 1-3 and 20 over Aldrich (U.S. Patent No. 6,008,164) in view of Deckman (U.S. Patent Application Publication No. 2003/0158055); and (2) claims 4-19 over Aldrich in view of Deckman and further in view of Wittenbrink (U.S. Patent No. 6,506,297). Applicants respectfully traverse each of rejections (1) and (2).

The lubricant base oil of claim 1 consists essentially of a normal paraffin and an isoparaffin, and satisfies the requirements: (a) an average carbon number N_c in one molecule is not less than 29 but not more than 35; (b) an average branch number N_b in one molecule, which is derived from a ratio of CH_3 carbon to total carbon determined by ^{13}C -NMR analysis and the average carbon number N_c in one molecule, is not more than $(0.2N_c - 3.1)$ but not less than 1.5; and (c) a viscosity index is 145-170 and a kinematic viscosity at 40°C is 17-25 mm^2/s .

The Patent Office alleges that Aldrich describes all of the features of claim 1 except above requirements (a) and (b) and the kinematic viscosity at 40°C being 17-25 mm^2/s , as recited in claim 1. The Patent Office alleges that Aldrich describes ranges that overlap or lie inside the ranges recited in above requirements (a) and (b) of claim 1 and that Deckman

describes the kinematic viscosity recited in claim 1. However, for at least the following reasons, the combination of Aldrich and Deckman would not have rendered obvious claim 1.

Neither Aldrich nor Deckman describe requirements (a) and (b) recited in claim 1. Further, even if Aldrich or Deckman describe a range that overlaps with the ranges recited in claim 1 as the Patent Office alleges, the combination of Aldrich and Deckman would not have rendered obvious claim 1 in view of the unexpected results of requirements (a) and (b) recited in claim 1. The Patent Office alleges that the claim ranges are optimized ranges that could have been found by routine experimentation. See page 7, lines 6-17 of the Office Action. Applicants respectfully disagree.

As discussed in the April 27, 2010 Supplemental Amendment, the above features (a) and (b) recited in claim 1 allow the lubricant base oil to have a high viscosity and a low pour point. Mr. Kobayashi's Rule 132 Declaration (Declaration) included with the April 27, 2010 Supplemental Amendment, and Table 2 of the specification, show by experiment that the claim ranges of Nc and Nb are required to allow for the recited viscosity index and to lower the temperature of the pour point.

As shown in Table A of the Declaration, having (a) an average carbon number Nc in one molecule of not less than 29 but not more than 35 and (b) an average branch number Nb in one molecule, which is derived from a ratio of CH₃ carbon to total carbon determined by ¹³C-NMR analysis and the average carbon number Nc in one molecule, of not more than (0.2Nc - 3.1) but not less than 1.5, is critical to achieving (c) a viscosity index is 145-170 and a kinematic viscosity at 40°C is 17-25 mm²/s, as recited in claim 1.

The combination of Aldrich and Deckman does not describe, or provide any reason or rationale for one of ordinary skill in the art to have come to, above features (a) and (b) recited in claim 1.

First, it is unexpected that the lubricant base oil of claim 1 has an average carbon number N_c in one molecule of not less than 29 but not more than 35 and also the kinematic viscosity at 40°C being 17-25 mm²/s. This unexpected result, as shown in the April 27, 2010 Rule 132 Declaration, and specifically in Table A therein (in conjunction with Table 2 of the present application) was extensively discussed in the April 27, 2010 Supplemental Amendment.

During the February 3 interview, the Patent Office alleged that the experimental evidence shown in Table A of the Declaration and Table 2 of the specification established unexpected results only for N_c values at the lower end of the claim range (i.e., a N_c of 29), and requested that further evidence be shown at the upper end of the claim range (i.e., a N_c of 35).

In response, Applicants provide the attached Journal article (Journal of the Japan Petroleum Institute, Vol. 48, No. 6, pages 365-372 (2005)). As shown in Fig. 14 of the Journal article, oil that has an average carbon number N_c of greater than 35 has a kinematic viscosity at 40°C of greater than 30 mm²/s, which is outside the range (17-25 mm²/s) of claim 1*. This additional evidence confirms that it is unexpected that the lubricant base oil of claim 1 has an average carbon number N_c in one molecule of not less than 29 but not more than 35 and also the kinematic viscosity at 40°C being 17-25 mm²/s.

Regarding requirement (b) of claim 1, the Patent Office alleges that Aldrich describes a range that overlaps with the recited range of claim 1, and thus requirement (b) of claim 1 would have been obvious. Applicants respectfully disagree.

Aldrich merely describes that the free carbon index of the branched paraffins is at least about 3 while the N_c may broadly be 20 to 40. See col. 2, lines 27-33 of Aldrich.

* As shown from Fig. 14 of the Journal, it is also not inherent that an oil having a average carbon number of 35 will also have a kinematic viscosity of 17-25 mm²/s.

Further, claim 1 requires a specific relationship between Nc and Nb, whereas Aldrich merely describes two independent, broad ranges for a free carbon index and a carbon number. There is no indication in Aldrich what Nb is for a given Nc value, and Aldrich describes no relationship between Nc and Nb. Thus, one cannot conclude that Aldrich describes a range that overlaps with claim 1, because claim 1 requires Nb to be based upon Nc.

The broad disclosure in Aldrich of a free carbon index does not describe or provide any reason or rationale for one of ordinary skill in the art to have come to an average branch number Nb in one molecule, which is derived from a ratio of CH₃ carbon to total carbon determined by ¹³C-NMR analysis and the average carbon number Nc in one molecule, of not more than $(0.2Nc - 3.1)$ but not less than 1.5, as recited in claim 1.

Still further, the unexpected results evidence rebuts any alleged overlap position taken by the Patent Office. Aldrich is even further removed from the claim ranges than the comparative examples of Table 2 of the specification and Table A of the Declaration. For example, Table 2 of the specification shows Comparative Example 1 having an Nc value of 28.2 (within the 20 to 40 range of Aldrich). At this Nc value, claim 1 would require Nb to be not more than 2.54 (calculated using $(0.2Nc - 3.1)$), but Comparative Example 1 has an Nb of 2.74, and a poor kinematic viscosity less than 17. As another example, as shown in Table A of the Declaration, Comparative Example A1 has an Nc value of 28.1 (within the range of Aldrich), but has a Nb value of 2.7, which is above the 2.52 value required by claim 1 at this value of Nc, and also has a poor kinematic viscosity. Accordingly, even if overlap were present, the evidence of record rebuts any prima facie obviousness on mere overlap alone.

Thus, the evidence shows unexpected results for claim 1 having an average carbon number Nc in one molecule is not less than 29 but not more than 35, an average branch number Nb in one molecule, which is derived from a ratio of CH₃ carbon to total carbon determined by ¹³C-NMR analysis and the average carbon number Nc in one molecule, of not

more than (0.2Nc - 3.1) but not less than 1.5, and also the kinematic viscosity at 40°C being 17-25 mm²/s.

As detailed above, the claimed relationship of features (a) and (b) are significant, and unexpected. Thus, Aldrich's disclosure that the free carbon index of the branched paraffins is at least about 3, in combination with a the broad carbon number of 20 to 40, does not render obvious the claimed range of not more than (0.2Nc - 3.1) but not less than 1.5, as recited in claim 1, and the unexpected results associated therewith.

Regarding the recited viscosity index of claim 1, the Patent Office admits that Aldrich does not describe a viscosity index of 145-170. Deckman does not remedy this deficiency of Aldrich. Deckman describes a Group II paraffinic oil* that is a hydrotreated oil having a viscosity of approximately 22.7 cSt at 40°C. See paragraph [0107] of Deckman. Deckman describes that the hydrotreated oil having a viscosity of 22.7 cSt at 40°C also has a viscosity index of 116. See Table 3 of Deckman. Thus, even if the hydrotreated oil having a viscosity of approximately 22.7 cSt at 40°C were to have been combined with Aldrich, the resulting base oil would have had a viscosity index of 116, which is below the claim range of 145-170 recited in claim 1.

Thus, Deckman does not describe a base oil having a viscosity index that is 145-170 and a kinematic viscosity at 40°C that is 17-25 mm²/s, as recited in claim 1. Thus, Deckman does not remedy the deficiencies of Aldrich.

* During the interview, the Patent Office alleged that the paraffinic oil of paragraph [0107] of Deckman is not the same as the oil in Table 3 of Deckman. However, Deckman, in paragraph [0107], describes a Group II base oil. Deckman further describes that Group II base oils have a viscosity index of less than 120. See the Base Stock Properties table in paragraph [0021] of Deckman. Thus, regardless of whether the Group II oil of paragraph [0107] of Deckman is shown in Table 3, it must have a viscosity index of less than 120, which is below and outside the recited range of claim 1 (i.e., a viscosity index is 145-170).

The combination of Aldrich and Deckman thus does not describe or render obvious the combination of requirements (a)-(c) recited in claim 1. Further, even if Aldrich or Deckman describe a range that overlaps with the ranges recited in claim 1 as the Patent Office alleges, the combination of Aldrich and Deckman would not have rendered obvious claim 1 in view of the unexpected results of the combination of requirements (a)-(c) recited in claim 1.

Claims 2-3 depend from claim 1. For at least their respective dependency, and for the additional features recited, the combination of Aldrich and Deckman also would not have rendered obvious claims 2-3.

Wittenbrink does not remedy the above described deficiencies of Aldrich and Deckman. Wittenbrink does not describe, or provide any reason or rationale for one of ordinary skill in the art to have come to, features (a)-(c), as recited in claim 1. Thus, the combination of Aldrich, Deckman and Wittenbrink would not have rendered obvious claim 1.

Claims 4-19 depend from claim 1. For at least their respective dependency, and for the additional features recited, the combination of Aldrich, Deckman and Wittenbrink also would not have rendered obvious claims 4-19.

In view of the above, withdrawal of the rejections (1) and (2) is respectfully requested.

Concluding Remarks

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. Favorable reconsideration and prompt allowance of claims 1-20 are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



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JAO:ABW/abw

Attachment:
Journal of the Japan Petroleum Institute article

Date: March 7, 2011

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[Regular Paper]

Viscosity Properties and Molecular Structure of Lube Base Oil Prepared from Fischer-Tropsch Waxes

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Lube base oils were prepared by hydrocracking/isomerization of Fischer-Tropsch synthesized waxes and long-chain α -olefins with various carbon chain lengths. Correlations between operation conditions, viscosity properties of base oil, and molecular structures were investigated. Prepared base oils showed very high viscosity indexes of up to 159, but these varied widely with the severity of the hydrocracking/isomerization conditions and feedstock. Viscosity indexes of base oil had a good correlation with the severity of the hydrocracking/isomerization conditions, that is higher conversion resulted in lower viscosity index. "Average branching numbers" were calculated from the average carbon numbers and the ratio of CH, CH₃ carbons obtained from ¹³C-NMR analysis, considering that the base oils mainly consisted of noncyclic paraffins. Increased conversion resulted in decreased average carbon number and increased average branching number with all feedstocks. Even with conversion of under 10%, about 2 branches per molecule were generated. On the other hand, the rate of generation of 3 or more branches was comparatively low. Average carbon number and average branching number also showed good correlations with the viscosity properties of the base oil such as kinematic viscosity and viscosity index. Viscosity indexes increased with higher average carbon number or lower average branching number. The effect of average carbon number or average branching number on the viscosity index depended on the feedstock, so a new index (average carbon number)² × (average branching number)⁻¹ was introduced as a molecular structural parameter of paraffins, and the index was confirmed to indicate the viscosity index regardless of the feedstock. A similar structural parameter (average carbon number)^a × (average branching number)^b was applied to kinematic viscosity. Kinematic viscosities at 40°C and 100°C showed good correlations when (a, b) = (3.5, 0.9) and (3.0, 0.5), respectively.

KeywordsFischer-Tropsch wax, α -Olefin, Isomerization, Lubricant base oil, Viscosity index, Average branching number**1. Introduction**

The increasing interests in environmental issues have boosted the demand for high efficiency clean fuel, that is, sulfur-free diesel oil or gasoline. This recent tendency has also required improvement in the properties of lubricant oil cleaner and more efficient as well. According to a recent survey¹⁾, the total demand for lube base oil has been almost constant during the past two decades, but the demand for high grade base oil (*i.e.* Group II or III) has gradually increased. Base oils prepared from paraffinic and clean source, such as Fischer-Tropsch (FT) synthesized paraffin, are becoming more attractive as these products mainly consist of noncyclic paraffins and have very high viscosity indexes²⁾. The Gas-to-Liquid project is now being developed all over the world^{3),4)} and high performance lube

base oil is expected to be a product from FT wax as well as clean fuel oil.

One of the most fundamental structural parameters of base oil is the carbon number distribution, but this parameter is too complicated to relate to the performance of base oil, so the average carbon number was taken as the parameter that represents the size of molecule. Another important structural parameter is the branching of the paraffin molecule. Base oil contains so many isomers that it is impossible to identify all isomers, for example by chromatography. One effective way to measure the branching of base oil is to investigate the CH₃ carbon or CH carbon ratio using ¹³C-NMR (nuclear magnetic resonance). Assuming that there is no quaternary carbon atom, the peaks of ¹³C-NMR can be assigned to CH, CH₂, or CH₃ carbon. Considering that base oil consists mainly of noncyclic paraffins, the average branching number can be calculated using the ratio of CH or CH₃ with average carbon number.

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Table 1 Properties of Feedstock

		FTW-1	FTW-2	AO-1	AO-2
Density/15°C	[g/cm ³]	0.809	0.817	0.825	0.848
Carbon number distribution		C18-35	C19-54	C20-36	C28-46
Iodine number	[g/100 g-oil]	N.A.	N.A.	73.9	39.1
Number of unsaturations	[mol/mol]	N.A.	N.A.	0.953	0.760
Distillation	IBP	316.0	343.0	336.5	430.0
properties [°C]	10%	379.0	401.0	343.5	449.0
(D 2887)	50%	416.5	474.0	368.5	494.5
	90%	456.5	524.0	431.5	562.0
	EP	488.5	580.5	521.0	610.0

N.A. = not analyzed.

The present study investigated the relationship between the hydrocracking/isomerization conditions, quality of base oil products, and molecular structures to design the base oil molecular structure and optimize the base oil production. Base oils were prepared from FT waxes and long chain α -olefins under various hydrocracking/isomerization conditions. The products showed a wide range of viscosity indexes from 114 to 159 depending on operation conditions. We focused on relating these two structural parameters to the operation conditions and viscosity properties of the base oil.

2. Experimental

2.1. Hydrocracking / Isomerization of Feedstock

FT waxes and long chain α -olefins were used as feedstock for the preparation of lube base oils. The carbon number distribution and other properties are shown in Table 1. Commercial isomerization catalyst HOP-302 (100 ml) developed by Japan Energy Corp. was filled in a fixed bed flow reactor with α -alumina (100 ml) as diluent. The hydrocracking/isomerization conditions were as follows: H₂ pressure 4.0-9.0 MPa, H₂/oil ratio 660-1500 N//l, operation temperature 340-370°C, liquid hourly space velocity, LHSV 0.33-1.00 h⁻¹. Before providing feedstock, catalysts were sulfided with gas oil solution containing 1 vol% carbon disulfide. Liquid samples were obtained after oil/gas separation.

2.2. Analysis of Base Oils

Distillation properties of product oils were evaluated with the ASTM D 2887 method to determine 360°C⁺ conversion defined as Eq. (1).

$$360^{\circ}\text{C}^{+} \text{ conversion (wt\%)} = \frac{(C_0 - C_1)}{C_0} \times 100 \quad (1)$$

where C_0 (wt%) = 360°C⁺ fraction of feedstock (2)

C_1 (wt%) = 360°C⁺ fraction of products (3)

Except when the n -paraffin content was under 1 wt%, product oils were dewaxed with mixed solvent (50% 2-butanone/50% toluene). Dewaxed samples were distilled with a TBP distillation apparatus and the bottom oils with boiling point above 360°C were taken as the

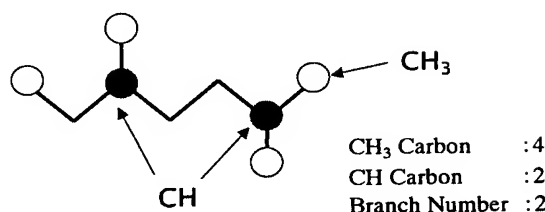


Fig. 1 Structure of 2 Branched Isoparaffin: Relationship of CH₃, CH Carbon Ratio and Branching Number

lube base oil samples.

Kinematic viscosities at 37.8, 40, 98.9 and 100°C were analyzed with the ASTM D 445 method. The Distortionless Enhancement by Polarization Transfer (DEPT) method was used to assign each peak of the ¹³C-NMR analysis of base oils to CH, CH₂, and CH₃ carbon assuming that quaternary carbon atoms were not present. Analysis was performed with a JEOL Ltd. GSX-270 NMR spectrometer with a 10 mm sample tube filled with approximately 50% of sample oil diluted with CDCl₃. Each peak was quantified by the analysis of ¹H gated decoupling without NOE, because the peak area obtained by the DEPT method is not quantitative.

2.3. Determination of the Structural Parameters of Isoparaffins

Average Carbon Numbers (ACNs): Average molecular weights were calculated from the kinematic viscosities at 37.8°C and 98.9°C by the ASTM D 2502-92 method. ACNs were calculated with Eq. (4), assuming that base oil samples in this study virtually consisted of only noncyclic paraffins with molecular formula of C_nH_{2n+2}.

$$\text{ACN} = (\text{average molecular weight} - 2)/14 \quad (4)$$

Average Branching Numbers (ABNs): The ABNs, were calculated with two methods. As shown in Fig. 1, ABN is equal to the average number of CH₃ carbons in one molecule minus 2 (Method A). ABNs can also be derived by counting CH carbon number in one molecule (Method B). Both CH₃ and CH carbon ratios were obtained from ¹³C-NMR analysis. ABNs

were calculated with the two methods and compared.

Method A: $ABN = ACN \times CH_3 \text{ carbon ratio} - 2$ (5)

Method B: $ABN = ACN \times CH \text{ carbon ratio}$ (6)

3. Results and Discussion

3.1. Properties of Prepared Base Oil

Most prepared base oils have very high viscosity indexes from 130 up to 159. However, one sample had a relatively lower viscosity index (113.8). These results suggest that it is important to optimize the operation conditions of the hydrocracking/isomerization reaction and to understand the molecular structure change during the preparation of high viscosity index lube base oils.

Analysis of FD-MS and iodine number confirmed that no olefins and a small amount of cyclic paraffins containing 1 naphthene ring were present in the prepared base oil. Figure 2 shows that at lower conversion under 40 wt%, the ratio of paraffins containing naphthene rings were very low, though at higher conversion ratio the content was relatively higher. This suggests that paraffins containing naphthene rings were generated in the process of isomerization. ^{13}C -NMR spectra (Fig. 3) or column chromatography indicated that the base oils did not contain aromatic compounds.

Based on these results, the molecular structures of base oils in this study were evaluated using 2 parameters

of isoparaffin, a parameter that represents molecular size (carbon number), and the state of branching.

3.2. Comparison of ABN by Method A and Method B

ABNs obtained by method A and method B are compared in Fig. 4. The good correlation suggests that the

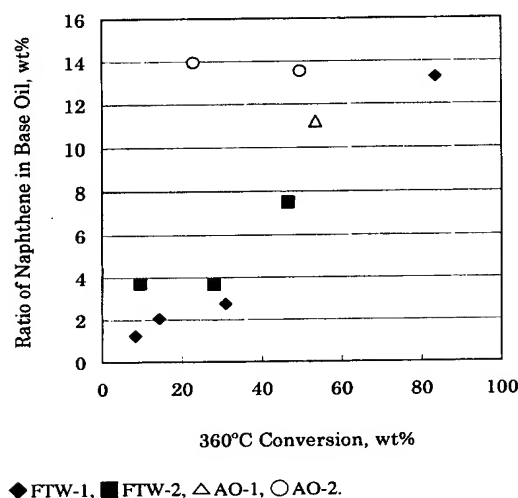
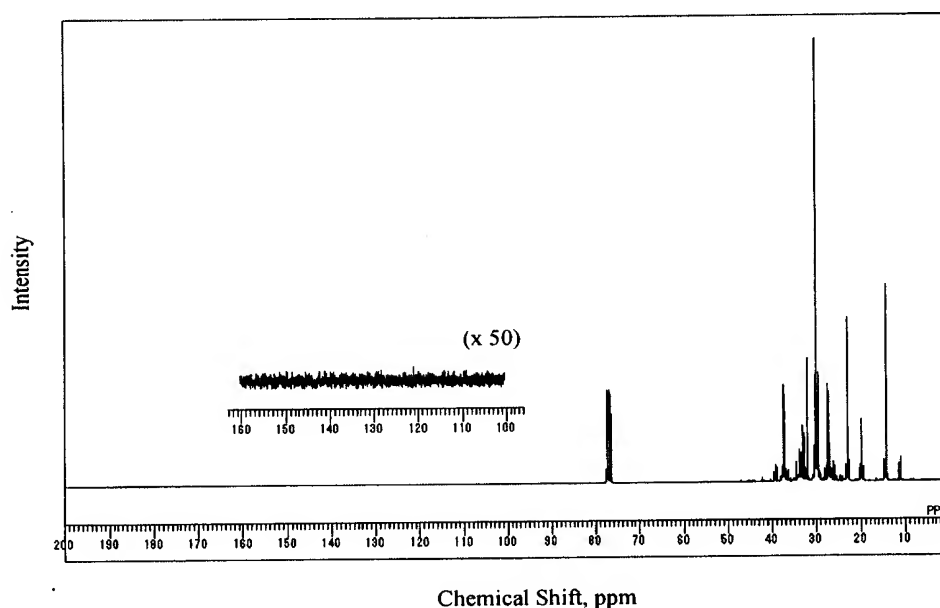


Fig. 2 Correlation between 360°C Conversion and Naphthene Content in Base Oil



Feedstock: FTW-1, hydrocracking/isomerization conducted under the following conditions.
 H_2 pressure: 9.0 MPa, H_2 /oil ratio: 1500 N//l, operation temperature: 350°C, LHSV: 0.44 h⁻¹.

Fig. 3 ^{13}C -NMR Spectrum of Lube Base Oil

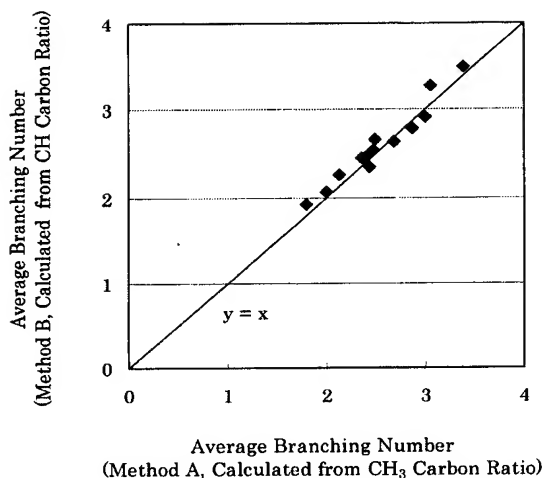
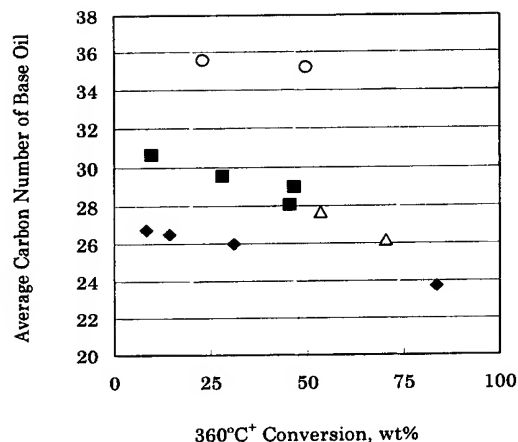
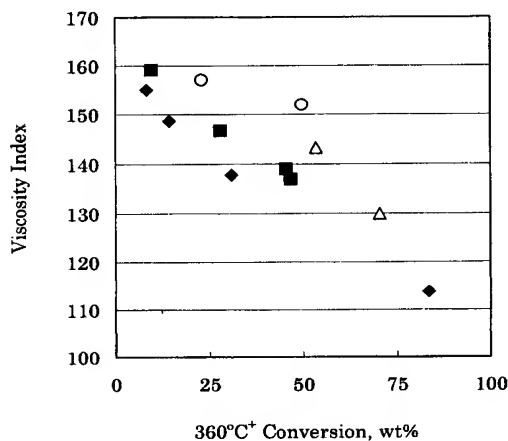


Fig. 4 Comparison of Average Branching Numbers Calculated from Method A and B



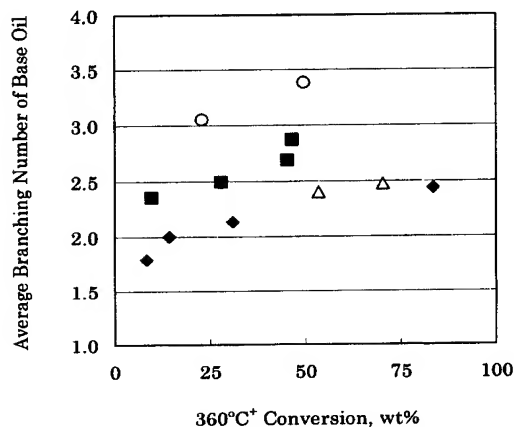
◆ FTW-1, ■ FTW-2, △ AO-1, ○ AO-2.

Fig. 6 Correlation between 360°C⁺ Conversion and Average Carbon Number of Base Oil



◆ FTW-1, ■ FTW-2, △ AO-1, ○ AO-2.

Fig. 5 Correlation between 360°C⁺ Conversion and Viscosity Index of Base Oil



◆ FTW-1, ■ FTW-2, △ AO-1, ○ AO-2.

Fig. 7 Correlation between 360°C⁺ Conversion and Average Branching Number of Base Oil

calculation method proposed in this report using analytical data of ^{13}C -NMR is reliable. ABNs obtained by these methods can be applied to the investigation of the molecular structure of isoparaffins in lube base oils. ABNs obtained of method A are the basis of the following discussion.

3. 3. Viscosity Index and Molecular Structure

Figure 5 shows the effect of the severities of the hydrocracking/isomerization reaction on the viscosity index of base oil. The viscosity index was drastically lowered with increased conversion with every feedstock. These changes can be attributed to structural

changes of the isoparaffins which form the base oils. 360°C⁺ conversion was varied by changing both operation temperature and liquid hourly space velocity, LHSV. However, properties of base oils or molecular structure changes could be described as a function of only 360°C⁺ conversion, that is 360°C⁺ conversion is the only index that represents the severity of the hydrocracking/isomerization reaction.

Figures 6 and 7 show the correlation of 360°C⁺ conversion with ACN and ABN, respectively. In the case of FTW-1, even at very low conversion (below 10 wt%), about 2 branches were generated (Fig. 7).

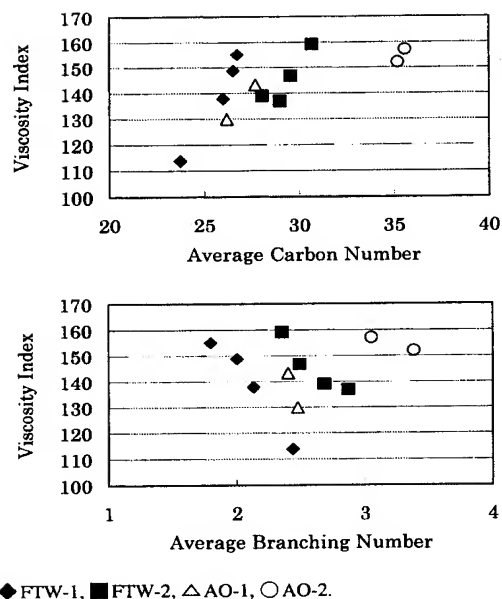


Fig. 8 Correlation between Average Carbon Number, Average Branching Number and Viscosity Index of Base Oil

With increased conversion, ABN increased up to 2.4 and other feedstocks showed similar trends. These results show that the formation of the first and second branches in the paraffin chain is a very quick reaction. On the other hand, the formation of the third and subsequent branches is comparatively slow. ACN tended to decline with increased conversion of all feedstocks (Fig. 6). This result indicates that the base oils became lighter.

These findings suggest some kind of correlation of ACN and ABN with the viscosity indexes as shown in Fig. 8 and correlation curves depend on the feedstock. These results indicate that both ACN and ABN are important factors for the viscosity index. Therefore, we attempted to describe viscosity indexes as a function of ACN and ABN with following Eq. (7).

$$\text{viscosity index} = f\{(\text{ACN})^a \times (\text{ABN})^b\} \quad (7)$$

Using $(a, b) = (2, -1)$ as multipliers, Eq. (7) and viscosity index showed good correlation as a quadratic curve regardless of used feedstock as shown in Fig. 9. This result shows that viscosity indexes of base oils prepared by hydrocracking/isomerization of waxy feedstock can be determined as a function of ACN and ABN. The obtained formula $(\text{ACN})^2 \times (\text{ABN})^{-1}$ was factorized as shown in Eq. (8) to analyze the adopted multipliers. The viscosity index can be expressed by multiplication of a function that expresses the size of the molecule (ACN) and a function that relates to the methylene chain length of the paraffin $((\text{ACN}) \times (\text{ABN})^{-1})$.

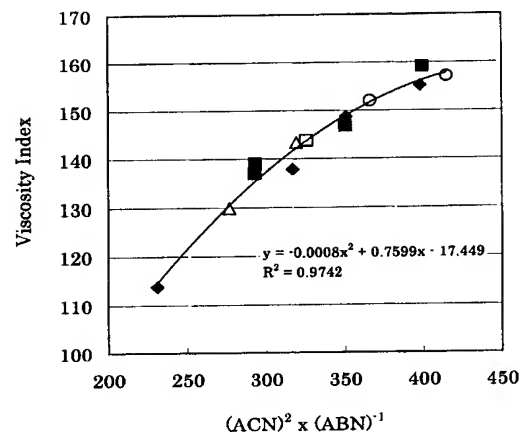
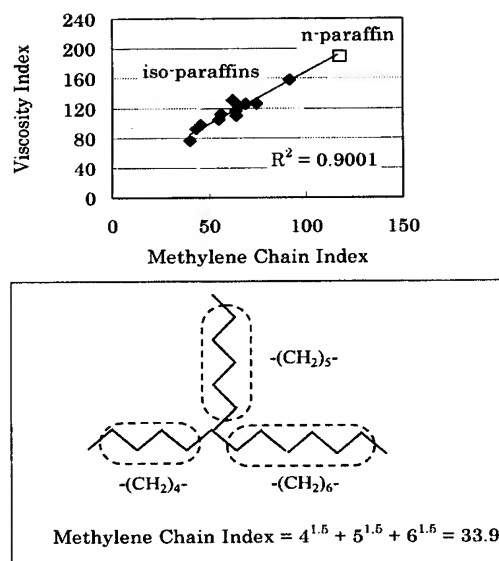


Fig. 9 Correlation between New Structural Parameter $(\text{ACN})^2 \times (\text{ABN})^{-1}$ and Viscosity Index of Base Oil

$$(\text{ACN})^2 \times (\text{ABN})^{-1} = \frac{(\text{ACN})^2}{(\text{ACN}) \times (\text{ABN})^{-1}} \quad (8)$$

It may seem a little strange that the viscosity indexes could be represented only by ACN and ABN, because the location of branches or the type of branches, such as methyl or ethyl or so on, strongly affect the viscosity properties of base oil⁵⁾. This result indicates that the location of branches or the type of branches have only a few variations in the case of hydrocracking/isomerization of Fischer-Tropsch paraffins or α -olefins. Reference 5) shows some properties of various kinds of hydrocarbons, such as kinematic viscosity or viscosity index. It is difficult to compare directly these data with the present results as the structures of some isoparaffins found in this reference are not practical in the case of base oils prepared from FT wax hydrocracking/isomerization, but the values can be of great help for understanding the result of our study.

As our results indicated that methylene chain length of paraffin is supposed to be an important factor for viscosity index, the influence of methylene length was investigated. A new molecular structural parameter that we call Methylene Chain Index was employed for this investigation. Methylene Chain Index = $\Sigma(ML^{1.5})$ where ML = methylene length. For example, the molecule shown in Fig. 10 has 4 carbon, 5 carbon, and 6 carbon methylene chains, so $\Sigma(ML^{1.5}) = 4^{1.5} + 5^{1.5} + 6^{1.5} = 33.9$. Figure 10 shows the correlation of Methylene Chain Index of several *i*-C26s and *n*-C26 with viscosity index, and indicates that longer methylene length is favorable for higher viscosity index. The influence of carbon number is also confirmed in Fig. 11. This



◆ isoparaffin, □ n-paraffin.

Fig. 10 Correlation between Methylene Chain Length Index and Viscosity Index of C26

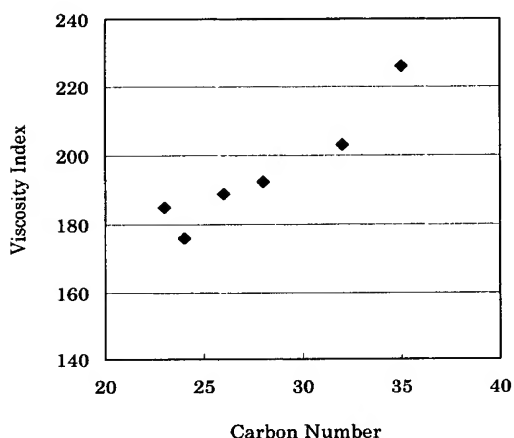
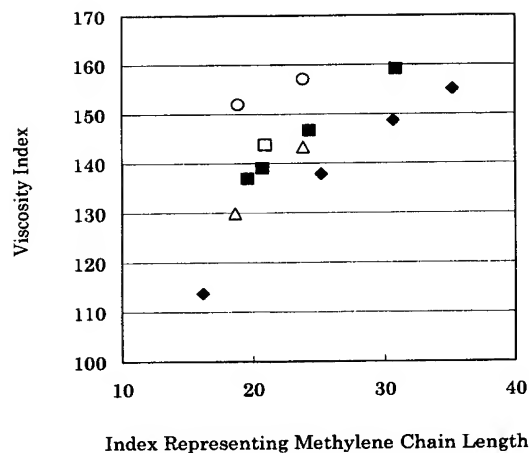


Fig. 11 Dependence of Viscosity Index of *n*-Paraffin on Carbon Number

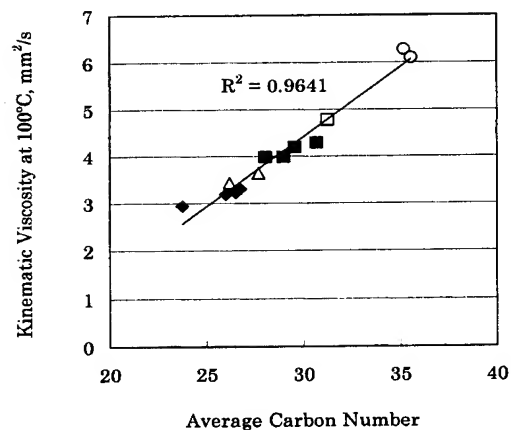
information explains the utility of Eqs. (7) and (8).

Matsuyama *et al.* proposed that the area of certain peaks of ^{13}C -NMR spectra relate to the methylene chain length of lube oil molecules prepared from crude oil and had good correlations with viscosity index⁶⁾. The same method was applied to the lube base oils of the present study and the correlation with viscosity index was evaluated. As shown in Fig. 12, the correlation between the proposed index and viscosity index strongly



◆ FTW-1, ■ FTW-2, □ FTW-2 (400°C cut), △ AO-1, ○ AO-2.

Fig. 12 Dependence of Viscosity Index on Methylene Chain Length



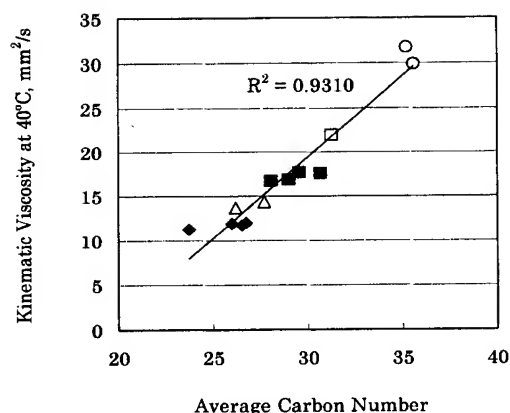
◆ FTW-1, ■ FTW-2, □ FTW-2 (400°C cut), △ AO-1, ○ AO-2.

Fig. 13 Correlation between Average Carbon Number and Kinematic Viscosity at 100°C

depended on the feedstock. This result strongly indicates that the size of the molecule is an important factor for viscosity index as well as methylene length and must be included in the structural parameters that represent viscosity index.

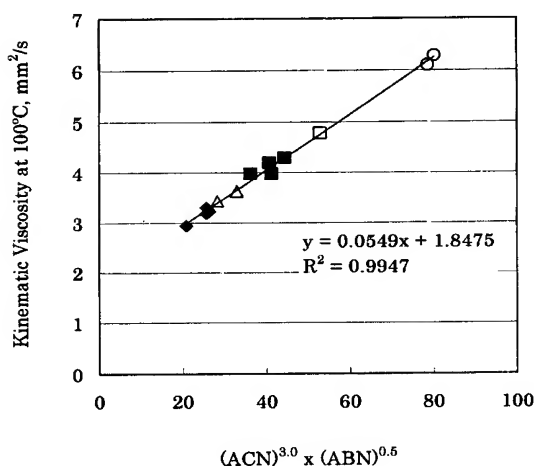
3. 4. Kinematic Viscosity and Molecular Structure

Figures 13 and 14 show the correlation between ACN and kinematic viscosity at 100°C and 40°C, respectively. Kinematic viscosity at 100°C had a good correlation with ACNs regardless of feedstock, but the correlation at 40°C seemed to be influenced by



◆ FTW-1, ■ FTW-2, □ FTW-2 (400°C cut), △ AO-1, ○ AO-2.

Fig. 14 Correlation between Average Carbon Number and Kinematic Viscosity at 40°C



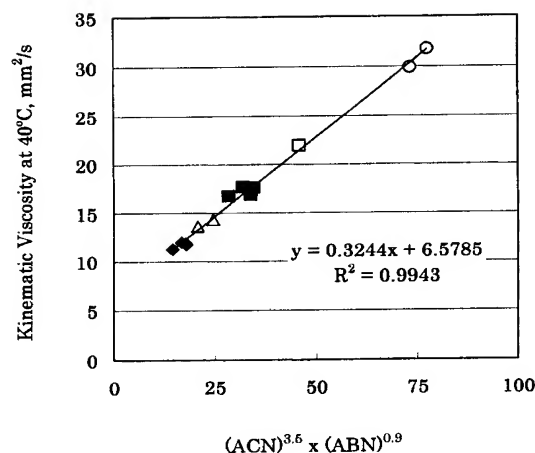
(ACN) = average carbon number, (ABN) = average branching number. ◆ FTW-1, ■ FTW-2, □ FTW-2 (400°C cut), △ AO-1, ○ AO-2.

Fig. 15 Correlation between Structural Parameter $(ACN)^{3.0} \times (ABN)^{0.5}$ and Kinematic Viscosity at 100°C of Base Oil

feedstock.

Therefore, a similar formula, $(ACN)^a \times (ABN)^b$ was applied to kinematic viscosities at both 40°C and 100°C. By employing $(a, b) = (3.5, 0.9)$ for the viscosity at 40°C and $(3.0, 0.5)$ for the viscosity at 100°C, good linear relationships between viscosity and molecular structural parameter $(ACN)^a \times (ABN)^b$ were obtained as shown in Figs. 15 and 16.

These results indicate that though molecular size is the dominant factor for kinematic viscosity, branching



(ACN) = average carbon number, (ABN) = average branching number. ◆ FTW-1, ■ FTW-2, □ FTW-2 (400°C cut), △ AO-1, ○ AO-2.

Fig. 16 Correlation between Structural Parameter $(ACN)^{3.5} \times (ABN)^{0.9}$ and Kinematic Viscosity at 40°C of Base Oil

state is also influential.

4. Conclusion

Lube base oils were prepared by hydrocracking/isomerization of Fischer-Tropsch synthesized waxes and long-chain α -olefins with various carbon chain lengths. Correlations between operation conditions, viscosity properties of base oil, and molecular structures were investigated.

(a) Viscosity indexes of prepared base oils widely varied from 114 up to 159 with severity of hydrocracking/isomerization reaction and feedstock used.

(b) Viscosity index decreased steeply with increased severity of hydrocracking/isomerization reaction with all feedstocks. The relationship between conversion and viscosity index depends on the feedstock.

(c) Average branching numbers (ABN) in one molecule were calculated from ^{13}C -NMR analysis and average carbon numbers (ACN). ABN increased and average carbon number (ACN) decreased with increased severity of hydrocracking/isomerization reaction with all feedstocks.

(d) ABN and ACN were applied to the description of viscosity properties of lube oils. The molecular structural parameter $(ACN)^2 \times (ABN)^{-1}$ showed good correlation with viscosity index. The correlation can be determined only with ABN and ACN and is independent of feedstock or operation conditions of the hydrocracking/isomerization reaction.

(e) The relationship between structural parameters and kinematic viscosities can be expressed by $(ACN)^a \times$

(ABN)^b adopting suitable multipliers *a* and *b*.

References

- 1) Gelder, A., Fourth ICIS-LOR World Base Oil Conference, London, 2000.
- 2) Igarashi, J., *Tribologist*, **48**, (4), 265 (2003).
- 3) Ondrey, G., *Chem. Eng.*, **111**, (5), 23 (2004).
- 4) Skrebowski, C., *Petroleum Review*, **691**, (58), 18 (2004).
- 5) Properties of Hydrocarbons of High Molecular Weight, API Research Project 42 Report, 1967.
- 6) Matsuyama, Y., Yagishita, K., Yoshida, T., 47th R&D Symposium of Jpn. Petrol. Inst., Tokyo, May 1998, Abstr., p. 49-50.

要 旨

Fischer-Tropsch ワックスの分解・異性化により製造した潤滑油基油の粘度特性と分子構造

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炭素数分布の異なる数種のフィッシャー・トロプシュ合成ワックス, および長鎖の α -オレフィンを水素化分解・異性化することにより潤滑油基油を調製し, 反応条件, 基油の粘度特性, そして潤滑油基油の平均分子構造の間の関係について検討した。

調製された潤滑油基油の粘度指数は, 最も高いもので159と非常に高い値を示す一方で, 反応条件や用いた原料により大きく異なった。調製された基油の粘度指数は分解・異性化反応のシビアリティー, すなわち分解率と良く相関し, 分解率が低いほど高い粘度指数を示した。得られた基油が主として非環状パラフィンから構成されることから, 基油の「平均炭素数」と¹³C-NMR分析から決定されるCH₃炭素またはCH炭素の比率より「平均分岐数」を導出した。いずれの原料油を用いた場合でも, 分解率の上昇とともに基油の軽質化および分岐の生成が進行する状況が定量的に観察された。分解率が10% 以下でも2

分岐/分子程度の分岐が生成しており, またそれ以上の分岐の生成速度は低いことがわかった。

また, 平均炭素数, 平均分岐数は, 動粘度, 粘度指数といった基油性状とも良い相関を示し, 粘度指数は, 平均炭素数が高いほど, また平均分岐数が小さいほど高い値を示した。

「粘度指数と平均炭素数」, 「粘度指数と平均分岐数」の関係は用いた原料により異なるものであったが, (平均炭素数)²×(平均分岐数)⁻¹式をパラフィンの構造パラメーターとして用いることにより, 粘度指数との関係を原料油によらず統一的に扱うことができた。

同様の構造パラメーター, (平均炭素数)^a×(平均分岐数)^b式を動粘度にも適用した結果, 40℃ および100℃ の動粘度は, それぞれ (*a*, *b*) = (3.5, 0.9), (3.0, 0.5) の時に構造パラメーターと良い相関を示すことがわかった。